

Application of ionic liquids as plasticizers for poly(methyl methacrylate)

Mark P. Scott,^a Christopher S. Brazel,^{*a} Michael G. Benton,^a Jimmy W. Mays,^b John D. Holbrey^c and Robin D. Rogers^{*c}^a Department of Chemical Engineering, The University of Alabama, Tuscaloosa, AL 35487, USA.

E-mail: cbrazel@coe.eng.ua.edu; Fax: +1 205 348 7558; Tel: +1 205 348 9738

^b Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA.

E-mail: JimmyMays@utk.edu; Fax: +1 865 974 9304; Tel: +1 865 974 0747

^c Center for Green Manufacturing and Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487, USA. E-mail: rdrogers@bama.ua.edu; Fax: +1 205 348 0823; Tel: +1 205 348 4323

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The room temperature ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, [C₄mim][PF₆] was found to be an efficient plasticizer for poly(methyl methacrylate), prepared by *in situ* radical polymerization in the ionic liquid medium; the polymers have physical characteristics comparable with those containing traditional plasticizers and retain greater thermal stability.

Ionic liquids (ILs)¹ have been studied as solvents for polymerization reactions.² Most recently, ILs have been shown to be good solvents for radical polymerizations.³ Relatively high solvent viscosity and support for long radical lifetimes have been suggested as factors enabling the formation of polymers with high molecular weights and controllable characteristics. In most cases, separation can be facilitated by the differential solubility of the polymers and monomers in the solvent, with the polymeric materials precipitating from the IL on formation.

ILs incorporated within porous polymer membranes, can act as supported polymer electrolytes.⁴ Rather than contacting polymer membranes with the IL and relying on a 'wetting' action, polymer-in-salt gel membranes have been prepared directly by polymerization of vinyl monomers in ILs⁵ and by polymerization of ILs incorporating polymerizable functions.⁶ It seemed likely that the formation of IL-polymer gels, such as are described by Watanabe and Mizumura,⁵ result from the plasticizing effects of the IL on the polymer matrix. The compatibility of some ILs with polymers can be advantageous in polymer processing to produce plasticized materials.

ILs containing imidazolium or pyridinium cations are similar to some conventional plasticizers, containing an aromatic core and pendant alkyl groups.⁷ Most plasticizers are based on three classes of compounds: phthalates, adipates, and trimellitates, with dioctyl phthalate (DOP) accounting for greater than 50% of all plasticizer used. Ideally, plasticizers exhibit most of the following characteristics: low volatility, low leachability, high and low temperature stability, thermodynamic compatibility with polymer, low cost and minimal health and safety concerns. ILs exhibit many of these characteristics, with performance, reproducibility, and wide thermal range being some of the greatest advantages over traditional plasticizing agents. With over 4 million tons of plasticizers produced annually,⁷ the development of novel plasticizing agents will yield alternatives for processing, and may expand the market to include a number of new applications.

Although the research presented here is focused on improved engineering properties of polymers, with an emphasis on high and low temperature stability imparted by the ionic liquids, the health and safety of plasticizers has been an important concern recently. Phthalate esters, including DOP, have come under scrutiny for potential health hazards,⁸ but are currently considered safe.⁹ Although collection of complete toxicity data for the [C₄mim][PF₆] ILs used in this work is still in progress, the reported LD₅₀ value for a related ionic liquid, 3-hexyloxymethyl-1-methylimidazolium tetrafluoroborate, has been reported as approximately 1400 mg kg⁻¹ in Wistar rats.¹⁰ This

compares with dioctyl phthalate which has an LD₅₀ value of 30 000 mg kg⁻¹ orally.

The objectives of this study were to determine the effect of ILs as plasticizers on the materials properties of poly(methyl methacrylate) (PMMA), as measured through the moduli of elasticity as a function of plasticizer type and concentration, thermal stability of PMMA samples determined at high temperatures, and glass transition temperature (*T*_g).

Polymer samples were prepared† by radical polymerization of MMA monomer in [C₄mim][PF₆] or DOP, initiated using AIBN. Plasticized PMMA samples formed readily in the presence of DOP and [C₄mim][PF₆] at up to 30 wt%. Beyond this concentration, the IL remained compatible with the polymer and allowed production of plasticized PMMA with 50 wt% IL, while samples prepared with initial DOP concentrations of 40 and 50 wt% plasticizer exhibited phase separation upon cooling after polymerization and did not produce uniform samples.

Glass transition temperatures were determined by DSC. The glass transition is important in design of polymeric materials because it marks the transition between hard, glassy properties at lower temperatures and rubbery behavior at higher temperatures. Plasticizers are often used to reduce the glass transition temperatures to make polymers workable and flexible at lower temperatures. In Fig. 1, the *T*_g of PMMA dropped significantly with only 10 wt% DOP, with only little change in *T*_g with additional DOP plasticizer. In contrast, the glass transition for the polymers incorporating [C₄mim][PF₆] displayed an almost linear decrease with IL content between 0–50 wt%. Bulk PMMA had a *T*_g around 120 °C, which drops linearly to nearly 40 °C with 50 wt% [C₄mim][PF₆] as a plasticizing agent, allowing greater specific control over polymer properties.

The elastic moduli for PMMA samples prepared in the presence of DOP and [C₄mim][PF₆] were determined at room temperature. The results (Fig. 2) show a decrease with increasing plasticizer content indicating that the IL does indeed act as an plasticizer for the polymer with a performance that is comparable with that of conventional plasticizers. With both

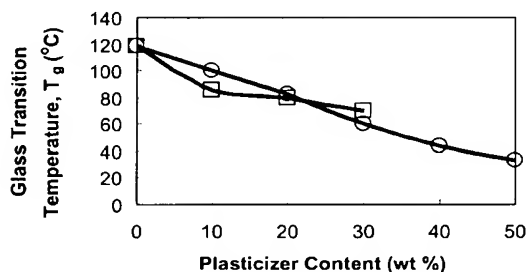


Fig. 1 Effect of DOP and IL plasticizers on the glass transition temperatures (*T*_g) of PMMA samples, determined by DSC for samples containing a range of DOP (□) and [C₄mim][PF₆] (○).

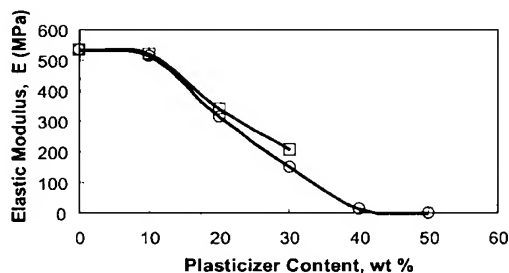


Fig. 2 Effect of plasticizer content on elastic moduli of PMMA samples plasticized with DOP (□) and [C₄mim][PF₆] (○). Standard deviations for multiple experiments are all smaller than the data symbols.

DOP and IL as plasticizers, the polymer maintains a high elastic modulus until sufficient (*i.e.* greater than 10 wt%) plasticizer was added, from which point, the elastic modulus decreases progressively with increasing plasticizer content. Because the IL could be successfully incorporated into PMMA at higher concentrations than for DOP, the IL allowed a continuing linear decrease in elastic modulus with increased plasticizer content. This allows control of polymer mechanical properties over a greater range than the traditional plasticizing agent. Further experiments to determine the effects of temperature and a range of ILs on the behavior of plasticized systems are underway.

One of the most important characteristics of plasticizer compounds is low volatility so that the polymer can remain flexible over a long lifetime without becoming brittle and failing. ILs are particularly intriguing in this aspect, as they typically have no detectable vapor pressure which could enable the formation of flexible materials with significantly extended lifetimes. TGA experiments were used to elucidate the mass loss from bulk and plasticized PMMA, as well as the IL and DOP by themselves (Table I). DOP has a boiling point of 380 °C, and is highly volatile at elevated temperatures, as evidenced by a 95% weight loss at 300 °C during a heat ramp of 10 °C min⁻¹. [C₄mim][PF₆] is essentially involatile at these temperatures, with an observed mass loss of only 1.15 wt% when subjected to the same heating profile. Because PMMA also begins to decompose at elevated temperatures, an evaluation of the bulk polymer showed a mass loss of 8.20 wt% at 300 °C during the temperature ramp. The presence of IL in the plasticized materials stabilized the polymer, resulting in a lower mass loss as the IL plasticizer content was increased. This contrasts remarkably with dioctyl phthalate, which causes a significant mass loss when DOP-plasticized PMMA samples are heated.

[C₄mim][PF₆] has better high temperature stability than a traditional plasticizer, DOP, when used with PMMA, allowing the polymer to have a wider range of usable temperatures.

Table I Thermal stability of plasticized PMMA, as determined by mass loss at 300 °C during a 20 °C min⁻¹ temperature ramp by TGA

Plasticizer Content	Mass Loss at 300 °C (wt%)
None (bulk polymer)	8.20
10% DOP	9.73
20% DOP	14.9
30% DOP	18.8
100% DOP (no polymer)	95.0
10% [C ₄ mim][PF ₆]	6.33
20% [C ₄ mim][PF ₆]	5.12
30% [C ₄ mim][PF ₆]	3.25
40% [C ₄ mim][PF ₆]	2.00
50% [C ₄ mim][PF ₆]	1.50
100% [C ₄ mim][PF ₆] (no polymer)	1.15

However, the hexafluorophosphate anion can decompose at high temperatures through hydrolysis, other ILs may provide superior thermal stability. In comparison to DOP, a greater amount of IL can be incorporated into PMMA, giving a greater range of elastic moduli for material design. The use of [C₄mim][PF₆] also showed a linear drop in the glass transition temperature, compared to DOP, which gave a much larger decrease in *T_g* at small plasticizer content. These results are promising for development of flexible polymeric materials that withstand a large range of working temperatures, with minimal evaporation or leaching.

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Notes and references

† Poly(methyl methacrylate), PMMA, was synthesized using varying ratios of monomer and either DOP or [C₄mim][PF₆]. Free radical polymerizations were carried out at 55 °C for 24 hours using 1 wt% AIBN as the thermal initiator. Samples containing no plasticizing agent, and 10, 20, 30, 40 and 50 wt% each of the IL or DOP were synthesized. The polymers were formed between two siliconized glass sheets with Teflon® spacers to provide samples of uniform thickness for mechanical testing. No extractions were done to remove solvents after polymerization. Small pieces were collected for calorimetry and thermogravimetric analyses (TA Instruments, model 2920 MDSC and model 2950 TGA, Newcastle, DE), and dog-bone shaped samples were cut for mechanical analysis using an automated materials testing system (Instron model 4465). TGA experiments were conducted using approximately 10 mg polymer samples exposed to a temperature ramp rate of 10 °C min⁻¹ up to 350 °C, where decomposition of the polymer was noted. Glass transition temperatures were determined by DSC, to 150 °C, using hermetically sealed aluminium pans. Mechanical tests were conducted using the dog-bone shaped samples at 25 °C using a strain rate of 5 mm min⁻¹ to measure the stress response as the PMMA samples were elongated.

- 1 J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156.
- 2 V. M. Kobryanskii and S. A. Arnaudov, *J. Chem. Soc., Chem. Commun.*, 1992, 727; V. M. Kobryanskii and S. A. Arnaudov, *Synth. Met.*, 1993, **55**, 1371; L. M. Goldenberg and R. A. Osteryoung, *Synth. Met.*, 1994, **64**, 63; S. A. Arnaudov, *Synth. Met.*, 1997, **84**, 295; M. F. Pinheiro, R. S. Mauler and R. F. de Souza, *Macromol. Rapid Commun.*, 2001, **22**, 425.
- 3 A. J. Carmichael, D. M. Haddleton, S. A. F. Bon and K. R. Seddon, *Chem. Commun.*, 2000, 1237; T. Biedron and P. Kubisa, *Macromol. Rapid Commun.*, 2001, **22**, 1237; M. G. Benton and C. S. Brazel, in *Ionic Liquids: Industrial Applications for Green Chemistry*, ed. R. D. Rogers and K. R. Seddon, ACS Symposium Series 818, American Chemical Society, Washington DC, 2002; H. Zhang, L. Bu, M. Li, K. Hong, J. W. Mays and R. D. Rogers, in *Ionic Liquids: Industrial Applications for Green Chemistry*, ed. R. D. Rogers and K. R. Seddon, ACS Symposium Series 818, American Chemical Society, Washington DC, 2002; K. Hong, H. Zhang, J. W. Mays, A. E. Visser, C. S. Brazel, J. D. Holbrey, W. M. Reichert and R. D. Rogers, *Chem. Commun.*, 2002, DOI: 10.1039/b204319j.
- 4 J. Fuller, A. C. Breda and R. T. Carlin, *J. Electrochem. Soc.*, 1997, **144**, L67; J. Fuller, A. C. Breda and R. T. Carlin, *J. Electroanal. Chem.*, 1998, **459**, 29; R. T. Carlin and J. Fuller, *Chem. Commun.*, 1997, 1345.
- 5 M. Watanabe and T. Mizumura, *Solid State Ion.*, 1996, **86**, 353.
- 6 H. Ohno, *Electrochim. Acta*, 2001, **46**, 1407.
- 7 D. F. Cadogan and C. J. Howick, 'Plasticizers' in *Kirk-Othmer Encyclopedia of Chemical Technology*, ed. J. I. Kroschwitz and M. Howe-Grant, Wiley, New York, 1992, 258.
- 8 A. H. Tullo, *Chem. Eng. News*, 2000, **78** (Dec. 4), 21.
- 9 B. Hileman, *Chem. Eng. News*, 2001, **79** (June 25), 12.
- 10 J. Pernak, A. Czepukowicz and R. Pozniak, *Ind. Eng. Chem. Res.*, 2001, **40**, 2379.